

Study of reversibility of ^{137}Cs selective sorption using direct measurement of radioactivity in the solid phase

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Abstract. A dynamic method is proposed to study the ^{137}Cs selective sorption kinetics using measurements of ^{137}Cs activity directly in the sorbent solid phase. For this purpose, the sorbent in the amount of 50 to 100 mg inside a disposable syringe membrane filter (MF) was eluted with ^{137}Cs solution containing K^+ and Ca^{2+} during 2-4 weeks. The desorption of ^{137}Cs was started by elution of the MF with the same solution but without ^{137}Cs . The activity of the sorbed ^{137}Cs is determined periodically by insertion of the same MF into the detector well of the gamma counter WIZARD 1480. During 15-50 days of desorption about 80-90% of the sorbed ^{137}Cs was eluted from soddy podzolic soils, palygorskite, bentonite, illite and dark fire-clay. For common building materials such as granite and asphalt about 60 and 70% of ^{137}Cs was desorbed after 7 days of sorbent elution by the solution having the potassium adsorption ratio 0.05. The non-desorbed fraction was a function of the ^{137}Cs interaction time. For example, for bentonite after 30 days of desorption about 10% of the sorbed ^{137}Cs was in the solid phase after 30 days of sorption and about 40% of the sorbed ^{137}Cs after 150 day of sorption.

1. INTRODUCTION

The highly selective sorption of ^{137}Cs in micaceous clay minerals takes place in the interlayer spaces near the frayed particle edges. Reversible partitioning of ^{137}Cs is believed to be substantial over the first few days following a contamination event, whereas irreversible sorption kinetics becomes important over time scales of weeks to months [1]. Madruga [2] has shown that significant fixation levels can be demonstrated within very short time intervals (days) after contamination, followed by a slow increase in fixation with time. It has generally been observed that K_d increases, and the exchangeability of ^{137}Cs bound to soil particles decreases, with increasing contact time between the radionuclide and the particles. These observations have been interpreted as a slow migration of ^{137}Cs from the frayed edge sites towards the deeper interlayer spaces between the illite layers, from where it cannot easily be released [3].

The exchangeability of soil-bound ^{137}Cs has been investigated by extracting soils with concentrated solution of ammonium salts ($0.1\text{--}1\text{ mol dm}^{-3}$) [2, 4]. These results suggest that such exchangeability measurements of ^{137}Cs underestimate the amount of the radionuclide that is actually taking part in ion-exchange with the soil pore solution. One of the main drawbacks of the methods based on the use of concentrated ammonium solutions is that they generate high levels of

^{137}Cs in the equilibrium solution, which in turn may become the rate-limiting factor for the radionuclide desorption from the solid phase.

The principle of the methods used by Wauters [5] and Madruga [2] is based on the generation of “infinite bath” boundary conditions and the monitoring of the ^{137}Cs desorption flux from the solid into the liquid phase at near zero ^{137}Cs activity. An adsorbent with ammonium copper hexacyanoferrate is often added directly to the solution. Desorption of ^{137}Cs is followed by monitoring the activity collected in the adsorbent. Madruga has shown [2] that the use of this method leads to the increase of the desorption yield by 10-15% as compared to the use of concentrated solutions. De Koning and Comans [4] has shown that this method increased the ^{137}Cs desorption yield from illite from 44-46 % to 85-90% in a short-term experiment.

Homoionic scenarios (K-, NH_4 -, Na-, or Ca-saturated samples) have been mainly used to study the ^{137}Cs desorption from natural sorbents. However, in soil pore solution there is a mixture of bivalent cations such as Ca^{2+} and Mg^{2+} and K^+ and/or NH_4^+ . The slow interlayer migration of Cs proceeds faster when the edges of illite are expanded by reaction with Ca^{2+} , relative to the collapsed structure of a K- or NH_4 -saturated illite [1]. The reversibility issue of the ^{137}Cs sorption from bionic solutions (i.g. K^+ and Ca^{2+}) is of importance because in natural waters these cations are the most important ones, and the ^{137}Cs desorption to the solutions is insufficiently investigated.

A methodology based on “infinite bath” boundary conditions is attractive but needs special equipment and experience. A new simple methodology is proposed based on flow-through experiments with small quantities of a sorbent placed inside the disposal syringe membrane filters and measurement of sorbed radioactivity directly in the solid phase. The goal of the study is to show the applicability of the method to study sorption and especially desorption kinetics of ^{137}Cs by soils, natural sorbents and building materials.

2. MATERIALS AND METHODS

2.1 Materials

The soils used include sod-podzolic sandy loam soil, (agricultural field, layer of 5-15 cm, v. Golubovka Belynichsky rayon of the Mogilyov oblast, Belarus) (SPS-1), sod-podzolic sandy soil (natural soil, a layer of 2-3 cm, horizon Oh, v. Zaborie Krasnogorsky rayon of the Bryansk oblast, RF) (SPS-2), Fithian illite (ILLITE) (Illinois, USA), palygorskite (PAL) from Borshchevo deposit and weathered dark-cherry bentonite (BEN) from Fersikovo deposit, dark fire-clay (DFC) from Ulianovo deposit of Kaluga region, RF. Asphalt (ASPH) and granite (GRN) were supplied from EPA USA in the frame of the ISTC project 4007. The sorbents were ground in a porcelain mortar and passed through a sieve with a mesh diameter of 0.25 mm except ASPH and GRN. ASPH and GRN were passed through a sieve with a mesh diameter of 0.125 mm. Physicochemical properties of the sorbents studied are shown in Table 1. The actual ($\text{pH}(\text{H}_2\text{O})$) and exchangeable ($\text{pH}(\text{KCl})$) acidity were determined by known procedures [6]. Organic carbon was determined by the wet combustion method [7]. The cation exchange capacity (CEC) was determined by the BaCl_2 method at pH 6.5 [8]. Lost on ignition (LOI) was determined at 1000 °C. Radiocesium interception potential relative to K^+ RIP(K) was determined according Wauters et al. [9]. The exchangeable fraction of selectively sorbed ^{137}Cs α_{Ex} was determined by extraction of a sorbent left after the determination of RIP(K) in the centrifuge tube with a 1 mol dm^{-3} ammonium acetate solution for 1 hour.

Table 1. Physicochemical properties of soils, absolute-dry weight.

Sample	pH		LOI, %	C _{org} , %	CEC, cmol(+) kg ⁻¹
	H ₂ O	KCl			
SPS-1	6.3	5.7	4.27±0.0 ₁	1.42±0.21	16.0±0.99
SPS-2	4.6	3.6	2.6±0.1	0.62±0.03	5.7±0.3
PAL	8.1	7.2	7.60±0.1 ₈	0.33±0.07	59.2±1.2
BEN	7.4	6.8	9.07±0.0 ₁	0.56±0.08	24.9±1.8
ILLITE	5.4	4.9	7.31±0.0 ₃	1.04±0.16	20.2±1.2
DFC	7.2	6.5	13.47±0.0 ₀₄	2.1±0.20	23.2±4.2
GRN	10.0	9.7	0.238±0.0 ₀₀₁	0.092±0.0 ₀₄	5.9±0.6
ASPH	9.6	9.5	5.56±0.0 ₂	2.92±0.03	19.3±0.7

2.2 Studying the kinetics of ¹³⁷Cs selective sorption and desorption using the direct measurement of radioactivity in the solid phase

For studying the ¹³⁷Cs selective sorption and desorption the dynamic method was used [10]. The method is based on the activity measurement of ¹³⁷Cs sorbed by a thin sorbent layer placed inside a polyethersulphone disposal syringe membrane filter (MF) under dynamic conditions. A sample (0.05–0.1 g of air dry sorbent) was placed in a MF (Acrodisk PN 4614) with a pore diameter of <0.45 µm and an outer diameter of 28 mm. The filter was eluted with a solution containing 100 mmol dm⁻³ Ca²⁺ and 0.5 mmol dm⁻³ K⁺ for 24 h using a peristaltic pump. The filter was then washed with a similar solution but containing 1 kBq dm⁻³ ¹³⁷Cs. Periodically, the ¹³⁷Cs activity was measured directly in the sorbent solid phase by placing the membrane filter in the detector well of the Wizard 1480 gamma counter. After the adsorption experiment was finished the ¹³⁷Cs desorption was determined by eluting the MF with a solution containing 100 mmol dm⁻³ Ca²⁺ and 0.5 mmol dm⁻³ K⁺.

3. RESULTS

The kinetics curves of ¹³⁷Cs selective sorption in natural sorbents, soils, and building materials are shown in Fig. 1. The sorbents studied differ considerably by their ability to sorb ¹³⁷Cs selectively. The maximal value of product K_dC_K for clay minerals ranges from 7 mol kg⁻¹ for PAL and BEN to 11 mol kg⁻¹ for ILLITE (Fig. 1a). The selective sorption of ¹³⁷Cs is considerably less in sod-podzolic soils and DFC (0.5–2 mol kg⁻¹), and minimal in the building materials (0.25 mol kg⁻¹) (Fig. 1b). The adsorption equilibrium is attained for PAL, DFC, SPS-2, GRN and ASPH during 2–5 days, for ILLITE during 15–20 days, and for BEN and SPS-1 sorption equilibrium is not achieved even for 30 days.

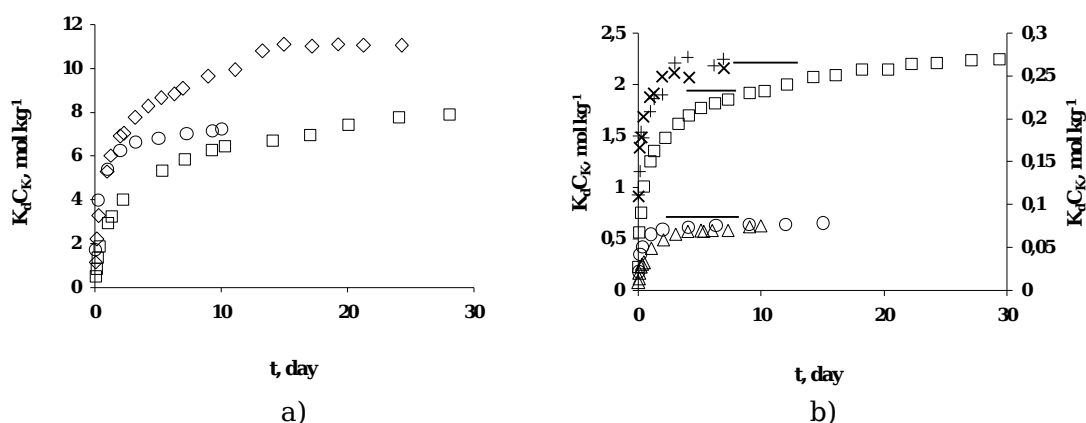


Figure 1. The kinetics of ^{137}Cs selective sorption by different sorbents: (a) \circ - PAL; \square - BEN; \diamond - ILLITE; (b) \circ - DFC; \square - SPS-1; Δ - SPS-2; $+$ - ASPH; \times - GRN.

The proposed method gives quite adequate results as compared to those determined by Wauters method [9]. Table 2 shows the maximal values of $K_d C_K$ product ($K_d C_{K\max}$) determined at the end of the ^{137}Cs sorption period (Fig. 1) and the $\text{RIP}(K)$ values determined by Wauters method [9]. These values are close to each other. The maximal difference is observed for illite ($K_d C_{K\max} = 11 \text{ mol kg}^{-1}$ as compared to $\text{RIP}(K) = 7.7 \text{ mol kg}^{-1}$).

The dynamic method was used to study the desorption of ^{137}Cs . Fig. 2a shows the desorption curves of ^{137}Cs eluted from the natural sorbents and soils and Fig. 3b shows those for asphalt and granite. Approximately 80-90% of the ^{137}Cs sorbed within 30 days can be removed during 15-50 days by a solution of 100 mmol dm^{-3} of Ca^{2+} and 0.5 mmol dm^{-3} of K^+ . Building materials more strongly retain the selectively sorbed ^{137}Cs . During 7 days about 40% of the sorbed radioactivity were fixed by granite, and about 30% by asphalt. The dependence of the desorbed fraction of ^{137}Cs on square root of

Table 2. Parameters of ^{137}Cs selective sorption, absolute dry weight.

Sample	$\text{RIP}(K), \text{mol kg}^{-1}$	$K_d C_{K\max}, \text{mol kg}^{-1}$	$\alpha_{\text{Ex}}, \%$
SPS-1	1.38 ± 0.14	2.26	30.9 ± 1.2
SPS-2	0.44 ± 0.07	0.63	28.1 ± 0.8
PAL	7.6 ± 1.0	7.2	6.8 ± 1.0
BEN	5.9 ± 0.2	7.8	13.5 ± 0.9
ILLITE	7.68 ± 0.05	11.0	15.2 ± 0.8
DFC	0.42 ± 0.02	0.65	22.5 ± 0.1
GRN	0.20 ± 0.02	0.26	5.8 ± 0.7
ASPH	0.28 ± 0.02	0.27	10.5 ± 1.1

time can be described by a straight line. This indicates that during the first several days the desorption of ^{137}Cs from soils and natural sorbents is a process controlled by diffusion.

The data shown in Fig. 2a suggest that the adsorption of ^{137}Cs by soils and natural sorbents aged for one month is almost completely reversible. However, extraction of sorbents aged for 1 day with 1 mol dm^{-3} ammonium solutions greatly underestimates the available fraction of ^{137}Cs . The exchangeable fraction of selectively sorbed ^{137}Cs α_{Ex} changes from 6-7% in GRN and PAL to 30% in sod-podzolic soils. This fact is usually attributed to the collapse of clay minerals interlayers. Therefore, the ^{137}Cs reversibility is considerably influenced by the slow process of ions exchange in micropores of sorbent particles. This process is controlled by diffusion. The diffusion rate influences both the processes of adsorption and desorption. In the Ca^{2+} rich environment the diffusion rate is high. Actually, the fixed ^{137}Cs fraction was found to be less than was expected earlier and for the natural sorbents aged during 30 days was about 10-15 %. However, if the interaction period of ^{137}Cs with a sorbent is increased, the value of a fixed fraction will also increase.

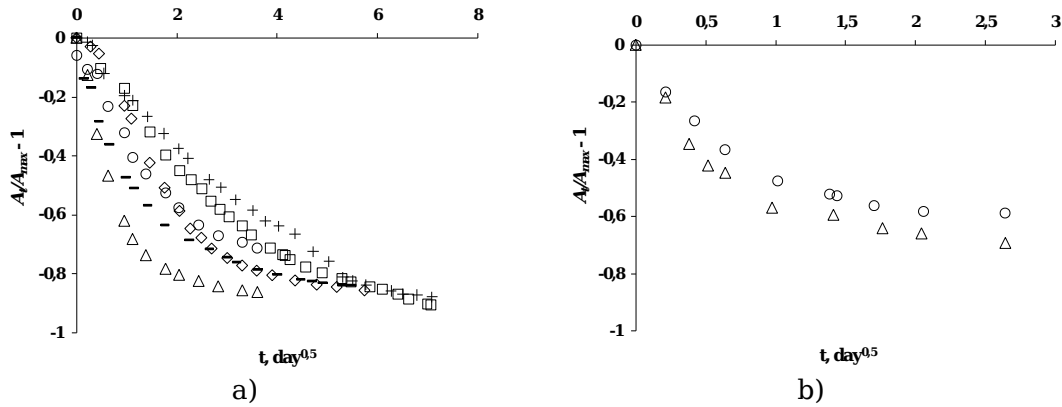


Figure 2. The kinetics of ^{137}Cs desorption by binary Ca-K solution from different sorbents aged with ^{137}Cs for 30 days: (a) Δ - DFC; \diamond - PAL; \square - BEN; \circ - ILLITE; $+$ - SPS-1; \blacksquare - SPS-2; (b) \circ - GRN; Δ - ASPH.

The aging of ^{137}Cs in weathered bentonite for 5 months led to an increase of the fixed ^{137}Cs fraction to 40% (Fig. 3). A plot of the ^{137}Cs fraction $A_t/A_{\text{max}} - 1$ desorbed by a solution containing $100 \text{ mmol dm}^{-3} \text{Ca}^{2+}$ and $0.5 \text{ mmol dm}^{-3} \text{K}^{+}$ versus square root of time can be described by two straight lines. These lines suggest the existence of two processes of ^{137}Cs desorption. Both of them are controlled by diffusion. The important result of the experiment is that even after 5 months of ^{137}Cs interaction with the weathered bentonite more than a half of the radioactivity is not fixed. The desorption process depends on the concentration gradient of ^{137}Cs .

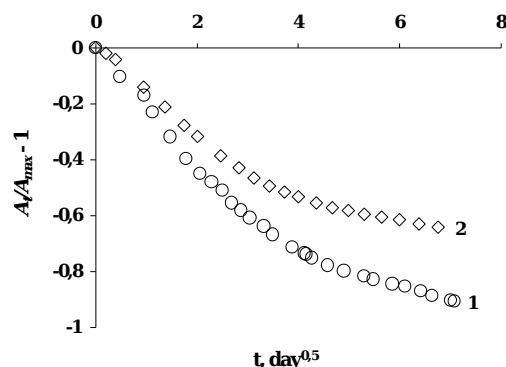


Figure 3. The kinetics of ^{137}Cs desorption from bentonite aged for 30 days (1) and 5 months (2).

4. CONCLUSION

A simple and efficient method to study ^{137}Cs reversibility is offered. This technique is based on the use of constant (adsorption) or zero (desorption) ^{137}Cs concentrations in the solution and consists in pumping through the sorbent and measurement of the sorbed ^{137}Cs activity directly in the solid phase. This method generates results which are close to those obtained by the methods based on the “infinite bath” scenarios.

The adsorption equilibrium is attained for PAL, DFC, SPS-2, GRN and ASPH during 2-5 days and for ILLITE during 15-20 days, while for BEN and SPS-1 aged for 30 days can be treated as practically reversible (80-90% was desorbed by the Ca-K solution). Building materials were found to bind ^{137}Cs stronger (the desorption yield is about 60-70%). Increasing the aging time from 30 days to 5 months lead to an increase in the fixed ^{137}Cs fraction from 10 to 40%.

The use of 1 M ammonium acetate to determine the exchangeable fraction of selectively sorbed ^{137}Cs leads to the marked underestimation of the fraction. The α_{Ex} for soils is about 30%, illite, bentonite, and asphalt is 11-15%, and for palygoskite and granite is 6-7%.

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